

Method for local Alitaton, Siliconization or Chromation of Metal Components

The invention relates to a method for the production of a locally limited diffusion layer on the surface of a metal component, whereby the diffusion layer is formed by the absorption of Si, Al and/or Cr into the surface of the metal component.

Mechanically and thermally highly stressed metal components usually are provided with protective layers which are intended to improve the wear protection properties or even improve thermal insulation properties. In order to improve bonding of these functional layers, it is common to provide a specially adapted adhesive layer between the component and the functional layer. Among other things, such adhesive layers must have a suitable chemical composition, and suitable roughness and surface topography. In so doing, a rough surface is advantageous in order to enhance the mechanical meshing of the later-applied cover layer, for example, a thermal insulation layer.

Referring to gas turbine technology, in particular, for example the production of turbine blades, adhesive layers are provided between the component and an outer thermal insulation layer. Suitable thermal insulation layers may be composed of (partially) stabilized ZrO_2 or even of other refractory oxides. In addition to being rough, the adhesive layers must be oxide-free and resistant to hot gas corrosion in order to be able to cling to the outer protective layers or the thermal insulation layer. Likewise, the adhesive layers must provide compensation for various thermal expansion coefficients of metal base materials and the thermal insulation layer.

In particular, diffusion layers containing Al and, optionally, additional transition metals, are well-suited as adhesive layers. In so doing, the selection of additive elements added to the diffusion layer, of course, depends significantly on the base material. Typically, the coating process for the production of diffusion layers is a powder pack process (Out of Pack Process). Referring to this, the coated surface is brought into contact with powders containing additive elements, hereinafter

also referred to as donor pack, and heated to a temperature at which a diffusion of the powder elements into the surface of the component can take place. The formation of the diffusion layers, generally referred to as alitiation (diffusion of aluminum), siliconization (diffusion of silicon), chromation (diffusion of chromium), etc., corresponds to the absorption of Al, Si or Cr.

For example, document DE 198 24 792 A1 describes a method for the production of a corrosion-resistant and oxidation-resistant layer, whereby a slurry containing at least one of the elements Cr, Ni or Ce is applied to a component and dried, and then alitiated at temperatures between 800°C and 1200°C.

Referring to document DE 3883 857 T2, a method has been known for the production of a diffusion layer of Al and other ferrite-stabilizing elements for steel. In so doing, a pack of Al or an aluminum alloy and other elements, a halide activator and optionally fillers is produced, and the steel component to be coated is embedded in this pack. Then diffusion coating takes place at temperatures above approximately 1000°C.

The described methods have the disadvantage that the formation of the diffusion layers cannot be locally limited. Rather, the entire component is provided with the diffusion layer in a non-specific manner. A sharp transition between the coated region and the uncoated component cannot be achieved. However, frequently a sharp boundary of the coated region is necessary. Therefore, the diffusion layer should be deposited only at locations where it is in fact required as the adhesive layer. Inasmuch as this layer significantly alters the surfaces or material properties, said layer can create significant disruptions of functionality in the remaining regions of the component.

Therefore, the object of the invention is to provide a method for the formation of diffusion layers on metal components, said method ensuring a local limitation of coated and uncoated regions in a simple manner.

In accordance with the invention, this object is achieved by a method for the production of a locally limited diffusion layer on a metal component by alitiation, siliconization and/or chromation, said method exhibiting the features of the characterizing portion of Claim 1, and by a use in accordance with Claim 8. Advantageous embodiments of the invention are the subject matter of dependent claims.

Therefore, in accordance with the invention, the diffusion layer is built up by means of a powder pack process, whereby, inside the packed bed reactor, at least one diffusion-blocking powder pack is provided in addition to the donor pack, said diffusion-blocking powder pack preventing the supply of additive elements to the uncoated regions of the metal component. In accordance with the invention, additive elements that are to be supplied by the donor pack are at least selected from Cr, Si and/or Al.

The inventive process comprises at least the following essential steps:

- a) application of a paste containing Cr, Si and/or Al—also referred to as a slurry depending on consistency—to the areas to be coated, in which case the paste also contains activators;
- b) solidification of the paste or slurry to form a donor pack;
- c) covering of the regions, which are not to be coated, with the diffusion-blocking powder pack;
- d) heating of the component and the powder packs to a temperature above 900°C, whereby alitiation, siliconization and/or chromation take place.

The paste or slurry that is required for the first step is essentially composed of additive elements, specifically Cr, Si and/or Al as their pure metals or as their alloys, of activators, binders and additional ballast substances.

The additive elements may be pure metals or even alloys. Frequently, it is advantageous to supply several additive elements simultaneously in the form of alloys (co-diffusion). Preferably, Al and Si are supplied simultaneously, with the quantity of Al far outweighing the quantity of Si.

Activators that are suitable in accordance with the invention include compounds which, under reaction conditions, may form volatile, specifically molecular, halides with the additive elements. Preferred activators are NH_4F , NH_4Cl or AlF_3 . It is also possible that at least part of the fluorides or chlorides are formed due to the decomposition of fluoridated or chlorinated organic binders or ballast substances.

Considering activators, ammonium halides are of particular interest, because the ammonia formed as a by-product occurs as reducing agent for metals. The undesirable oxidation of metals is thus suppressed.

Essentially, the usual organic binders used in the preparation of pastes or slurries are used as the binders.

Following are examples of solids compositions of the slurries or pastes in accordance with the invention. These compositions are intended to simply explain the subject matter of the invention in detail and are by no means to be understood as being restrictive. The stated numerical values are to be understood as being approximate.

Solids for paste for alitiation:

Powder of Al, AlSi, AlTi, AlCo and/or AlCr:	5–50 wt. %
Powder of Al_2O_3 :	5–50 wt. %
Organic binder:	1–15 wt. %
Activator of NH_4F and/or NH_4Cl :	0.5–2 wt. %

Solids for pastes for siliconization:

Powder of Si:	5–50 wt. %
Powder of Al_2O_3 :	5–50 wt. %

Organic binder:	1–15 wt. %
Activator of NH_4F and/or NH_4Cl :	0.5–2 wt. %

Solids for paste for chromation:

Powder of Cr:	5–50 wt. %
Powder of Al_2O_3 :	5–50 wt. %
Organic binder:	1–15 wt. %
Activator of NH_4F and/or NH_4Cl :	0.5–2 wt. %

Typically, the solids are mixed with water and/or alcohols and worked to result in a paste or a slurry. In conjunction with this, preferably a paste having the consistency of a plastically moldable material is prepared.

The organic binders may also be liquid compounds, of course.

During the continued process the paste or slurry is applied to the coated regions and solidified.

Typically, solidification is achieved by drying in an oven or the like.

As a result of this, a firm donor pack adhering to the surface of the metal component is formed.

Referring to an advantageous embodiment of the inventive method, at least the surfaces of the metal component, which later will be in contact with the powder pack or extend into the packed bed reactor, are provided with a separating layer. The separating layer is to facilitate the subsequent detachment of the powder packs after the formation of the diffusion layer. The separating layer is formed by a porous material which is largely inert to the base metal and the additive elements. Preferably, the separating layer is a thin layer of refractory oxides, specifically Al_2O_3 . Generally, the layer thickness is at approximately 0.02 mm to 3 mm.

The separating layer may be applied by conventional coating processes in order to form thick layers. Considering a preferred variant, a slurry is applied, for example, by spreading, immersion or spray-depositing. The slurry essentially consists of Al_2O_3 and binder.

During the subsequent method step (c), the component provided with the packed bed is introduced at least partially in a packed bed reactor.

The inventive arrangement of the packed bed reactor will be explained in detail with reference to Fig. 1, in which case the illustration represents only one of any number of potentially inventive variants.

Fig. 1 shows the alitation of damper pockets of a turbine rotor in a packed bed reactor (1) with the turbine rotor end (2), whereby its blade footing (3) extends into the packed bed reactor and is coated with a separating layer (4) of Al_2O_3 , and further shows the donor pack (5) arranged around the damper pockets, and the diffusion-blocking powder pack (6).

Preferably, the reactor (1) is a simple device for holding the component and for accommodating the powder fill or the diffusion-blocking powder pack. For example, the reactor may be designed as a metal capsule, into which extends the coated region of the component. Thereafter, the component (3) having coated and adjacent uncoated regions, as well as the donor pack (5), are covered with the diffusion-blocking powder pack (6).

The diffusion-blocking powder pack has the inventive effect of retaining or bonding the volatile compounds of the additive elements, so that a coating of the surfaces of the metal component not directly in contact with the donor pack is suppressed or completely avoided. The material responsible for the diffusion-blocking effect of this powder pack is metals which are capable of chemically bonding the additive elements. Typically, Ni, Co and/or Fe alloys are used in conjunction with this. Preferably, the diffusion-blocking powder pack contains metal powders having a similar or the same composition as the metal component to be coated. As a result of

this, the contamination of the metal component with elements of the diffusion-blocking powder pack is avoided. Ni or Ni alloys are particularly preferred.

In accordance with the invention, additional components of the diffusion-blocking powder pack are activators. In so doing, the same or even different activators than those used in the donor pack may be selected. Due to the presence of the activators in the outer powder pack, the activator loss occurring during the diffusion reaction is advantageously reduced in the region of the donor pack.

A preferred composition of the diffusion-blocking powder pack consists of a minimum of 50% of metal powder and of an activator content within the range of 0.2 and 5 wt.%. Additional components may be inert substances, such as, for example Al_2O_3 .

Finally, the actual diffusion coating takes place in the packed bed reactor. To do so, the reactor is heated to a temperature above 900°C . Preferably, the reactor is run with inert or protective gas, whereby Ar and/or H_2 are particularly preferred. As a result of the reducing conditions under H_2 , specifically the oxide formation is prevented, or at least partially reversed.

In this method step, preferably an alitiation, siliconization and/or chromation is performed.

The selection of process temperatures and process times are a function of the selected components, the donor packs and the desired layer consistency. Considering Cr base alloys, Ni base alloys or Co base alloys, the process temperatures used for alitiation are typically in the range of 750°C to 1200°C with holding times of 1 h to 20 hrs; for chromation, this is typically between 900°C and 1200°C with the same holding time.

Optionally, the metal components may already have metal coatings. As a result of this, optionally, a minimal adaptation to the process parameters—compared with those of uncoated components—may be necessary. However, the essential features of the inventive method basically remain unchanged.

The chemical components required for the surface treatment are formed inside the reactor, i.e., *in situ*. In so doing, the formation or decomposition of gaseous metal halides plays a substantial part

in transporting the metals determined for diffusion from the packed bed to the surface of the metal component.

The metal halides are formed *in situ* by halide-containing activators. The metal halides which reach the areas of the diffusion-blocking powder pack are bound by metal powder and prevented from diffusing into the uncoated regions.

Example:

Following is a description of an example of the alitination of a rotor blade for gas turbines that is locally restricted to the region of the damper pockets:

In order to prepare an alitination paste, 10 g of Al_2O_3 powder (wetable powder), 10 g of Al powder and 0.2 g of NH_4F were mixed, and then a paste was formed by admixing a binder-containing alcoholic water solution.

As a result, the paste had a kneadable consistency. The paste was pressed on the damper pockets and dried at approximately 50°C in a forced air oven. Referring to Fig. 1, the thusly conditioned rotor blade was fitted into a metal box, with only the blade end projecting into the packed bed reactor formed in this manner. The penetration site of the blade was sealed with some paste. Thereafter, the reactor was filled with diffusion-blocking cover powder (powder pack) to approximately double the height of the damper pockets. This powder pack was composed of Ni base material powder and 1 wt.% of NH_4F .

Alitination took place at a starting temperature of 1080°C and at a holding step at 1050°C and a duration of 4 hrs. The protective gases used for rinsing were Ar and H_2 .